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Characterization of the Relationship of the Cure

Cycle Chemistry to Cure Cycle Processing Properties

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DYNAMIC DIELECTRIC ANALYSIS: MONITORING THE CHEMICAL AND PHYSICAL CHANGES DURING CURE OF THERMOSETS AND THERMOPLASTICS

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INTRODUCTION

Dynamic Dielectric measurements made over a wide range of frequency provide a sensitive and convenient means for monitoring the cure process in thermosets and thermoplastics. Dielectric measurements are of particular importance for quality control monitoring of cure in complex resin systems because the measurement of dielectric relaxation is one of only a few instrumental techniques available for studying molecular properties in both the liquid and solid states. Furthermore, it is probably the only convenient experimental technique for studying the polymerization process continuously, that is, to examine the cure chemistry throughout the process of going from a monomeric liquid of varying viscosity to a crosslinked, insoluble, high temperature solid.

The major long-range objective of our research is to develop on-line dielectric instrumentation for quantitative nondestructive material evalua- tion and closed loop "smart" cure cycle control. The key to achieving this goal is to relate the chemistry of the cure cycle process to the dielectric properties of the polymer system by correlating the time, temperature, and frequency dependent dielectric measurements with chemical characterization measurements. Measurement of the wide variation in magnitude of the complex permittivity with both frequency and state of cure, coupled with chemical characterization work, have been shown in our laboratory to have the poten- tial to determine: resin quality, composition and age; cure cycle window boundaries; onset of flow and point of maximum flow; extent of and completion of reaction; evolution of volatiles; T_g; crosslinking and molecular weight buildup [1-5].

EXPERIMENTAL

The equipment and procedures for performing these experiments have been described in detail elsewhere [4,5]

THEORY

Measurements of C and G were used to calculate the complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$

$$\epsilon' = \frac{C \text{ material}}{C_o} \tag{1}$$

$$\epsilon'' = \frac{G \text{ material}}{C_o 2\pi f}$$

This calculation is possible when using the probe we have designed whose geometry is invariant over all measurement conditions. Both the real and the imaginary parts of ϵ^* can have a dipolar and an ionic component [7].

$$\epsilon' = \epsilon'_d + \epsilon'_i$$

$$\epsilon'' = \epsilon''_d + \epsilon''_i \tag{2}$$

The dipolar component arises from rotational diffusion of molecular dipole moments. The frequency dependence of the polar component may be represented by the Cole-Davidson function:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{(1+i\omega\tau)^\beta} \tag{3}$$

where ϵ_o and ϵ_∞ are the limiting low and high frequency values of ϵ, τ is a

a characteristic relaxation time and β is a parameter which measures the distribution in relaxation times. This term dominates the dielectric signal at high frequencies and in highly viscous media.

The ionic component, ε_i^*, often dominates ε^* at low frequencies, low viscosities and/or higher temperatures. The presence of mobile ions gives rise to localized layers of charge near to electrodes. Since these space charge layers are separated by very small molecular distances on the order of A^0, the corresponding space charge capacitance can become extremely large, with ε' on the order of 10^6 . Johnson and Cole, while studying formic acid, derived emperical equations for the ionic contribution to ε^*[8]. In their equations, these space charge ionic effects have the form

$$\varepsilon_1' = C_o Z_o \sin \frac{(n\pi)}{2} \omega^{-(n+1)} \ (\frac{\sigma}{8.85\times10^{-14}})^2 \tag{4}$$

where $Z^* = Z_o(i\omega)^{-n}$ is the electrode impedance induced by the ions and n is between 0 and 1 [7-9]. The imaginary part of the ionic component has the form

$$\varepsilon_o'' = \frac{\sigma}{8.85\times10^{-14}\omega} \ C_o Z_o \cos\frac{(n\pi)}{2}\omega^{-(n+1)}(\frac{\sigma}{8.85\times10^{-14}})^2 \tag{5}$$

where σ is the conductivity (ohm^{-1} cm^{-1}), an intensive variable, in contrast to conductance G(ohm^{-1}) which is dependent upon cell and sample size. The first term in Eq. 5 is due to the conductance of ions translating through the medium. The second term is due to electrode polarization effects. The second term becomes increasingly significant as the frequency of measurement is decreased.

RESULTS AND DISCUSSION

The real (ε') and imaginary (ε'') components of the complex permittivity (ε^*) as a function of frequency and temperature are used to monitor the physical state of a thermoplastic.

Figures 1 and 2 show dielectric results for two heating-cooling cycles for the polyimide thermoplastic LaRC-TPI [10] at 500 Hz and 1 MHz. The plots are quite different for these two frequencies. Clearly it is necessary to take data over a wide range of frequency to obtain sufficient information to interpret the results accurately. Figure 1 shows the temperature dependence of ε' for the initial heating and subsequent cooling cycle of the thermoplastic. The signal remains very low until the initial softening at 230°C wets the probe. Above the T_g of ~252°C a second sharp rise in ε' denotes the α peak. During cool down ε' decreases relatively rapidly with temperature until the resin solidifies. The point at which dipoles and ions cease being able to move with the applied oscillating electric field is dependent upon the frequency of measurement.

Figure 2 shows ε'' vs. temperature data for a second heating-cooling curve of the polyimide sample. At the lower, 500 Hz, frequency the loss is sensitive to the evolution of absorbed water (loss maximum at ~85°) and residual solvent (diglyme) evolution (loss maximum at ~160°) as well as the α peak just above T_g. At 1 MHz only the α peak can be observed.

Figures 3 and 4 show dielectric data for a poly(arylene ether) thermoplastic (PAE). Figure 3 is a plot of the loss, ε'' vs. temperature. The frequency dependent α peak can be seen just above the T_g of 142°C. The amplitude of this peak does not vary with frequency, but it becomes broader and the temperature of the maximum amplitude increases with increasing frequency. At higher temperatures another rise in ε'', often due to ionic phenomena, can be seen. This response also occurs sooner and is more pronounced at the lower frequencies.

A master curve for PAE using log ε'' vs. log frequency, has been constructed from the dielectric data taken between 147° and 279°C (Figure 4). The plot provides dielectric information on PAE over an effective frequency range much broader than that any single instrument can provide in the time or frequency domain alone. The fact that all of the curves are super-

imposable upon each other suggests that the same processes are responsible for the dielectric response in this temperature range. In this representation the ionic contribution is evident at the lowest frequencies - highest temperatures, the α peak is well defined, and the low frequency end of a β peak can be seen in the highest frequency-lowest temperature region of the plot.

Figures 5-8 show dielectric results for the crosslinking of a polyester resin by a free-radical mechanism. No external heat has been added; the temperature curve monitors the reaction exotherm. As shown in Figure 5, the permittivity of the resin drops during the course of the reaction. The onset of the reaction determined dielectrically (labeled "A" in the Figure) corresponds with the beginning of the reaction exotherm. An expansion of Figure 5 is shown in Figure 6. It can be used to monitor the slow final curing stage of the reaction.

Plots of Log (ε " $\cdot$ f) as in Figure 7 can be used to monitor the viscosity of the system. Early in the reaction the low frequency curves are all superimposable. In this region the first term in Eq. 5 dominates the signal. In work on other systems we have shown that during regions where this is so, the magnitude of this quantity is inversely proportional to the viscosity [11]. The point "B" where these curves diverge is near the gel point where solid-like diffusion controls both the mobility of the charged species and the rate of the reaction of the resin. The master plot for this data, Figure 8, shows the low frequency (f^{-1}) ionic contribution and a very shallow high frequency-long time relaxation peak, seen as a shoulder on the ionic portion of the curve. The position along this curve of a set of data can be used to monitor the extent of reaction.

CONCLUSIONS

Frequency dependent dielectric measurements can be used to monitor the cure process of thermoplastics including flow, T_g, evolution of moisture and residual solvent as well as their regenerative processing properties.

For thermosets, dynamic dielectric analysis permits detection of the onset of cure, the extent of cure, the viscosity and the onset of gel. The creation of a time-temperature master plot can be used to monitor reproducability during the cure and to determine the reaction extent at a given time and temperature during the cure process.

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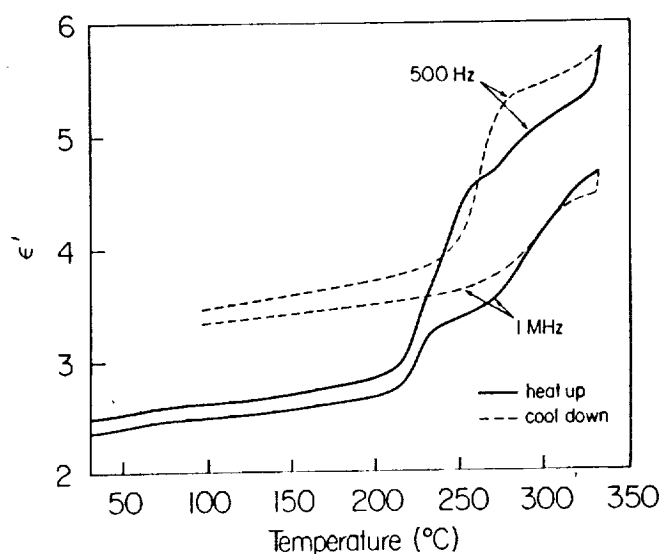
ACKNOWLEDGEMENT

Fig. 1. ϵ' vs. temperature for an initial heating and cooling cycle for LaRC-TPI. Wetting of the gauge at ~230°C as well as the α peak above T_g can be seen.
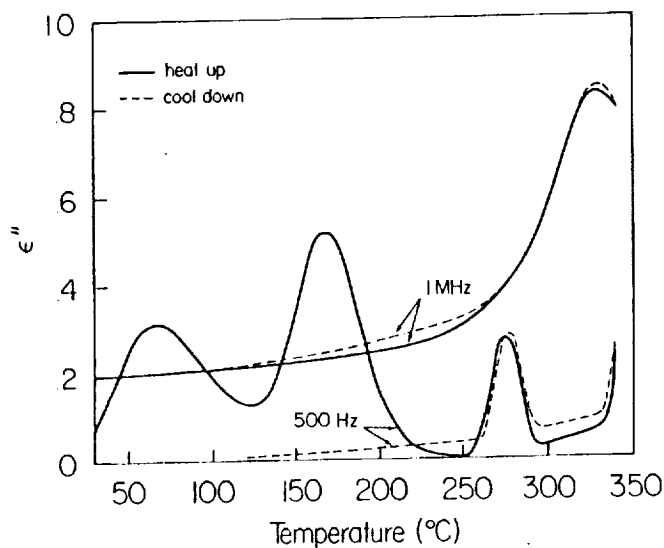
Fig. 2. ϵ'' vs. temperature for a second heating and cooling cycle of the sample of Fig. 1. Absorbed moisture, solvent evolution and the α peak can all be seen at 500 Hz; only the α peak is observed at 1 MHz.
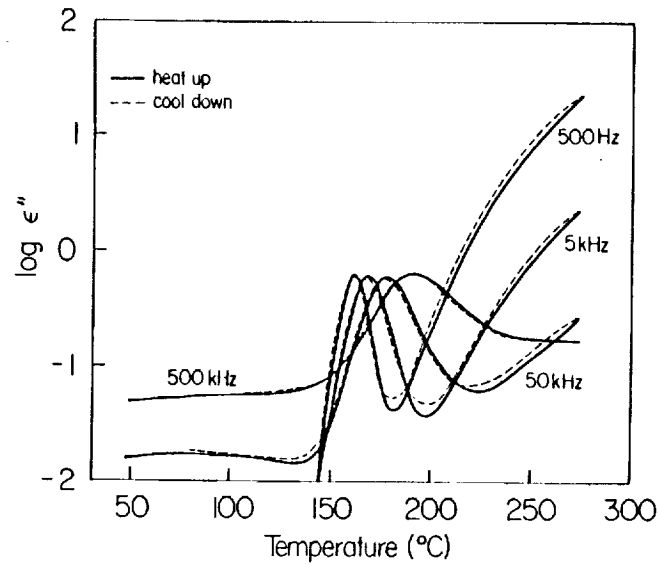
Fig. 3. Log ε'' vs. temperature for PAE film at multiple frequencies showing the α peak just above T_g and a high temperature ionic conduction.
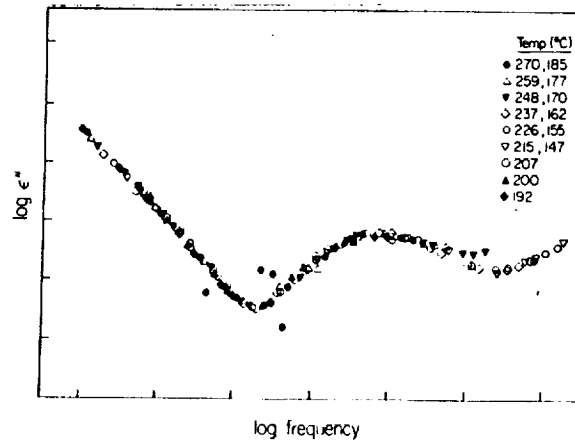

Fig. 4. A master curve or relative log ε'' vs. log frequency above T_g for PAE. A well defined α peak can be distinguished from low frequency-high temperature ionic phenomena and high frequency-low temperature β dispersion.
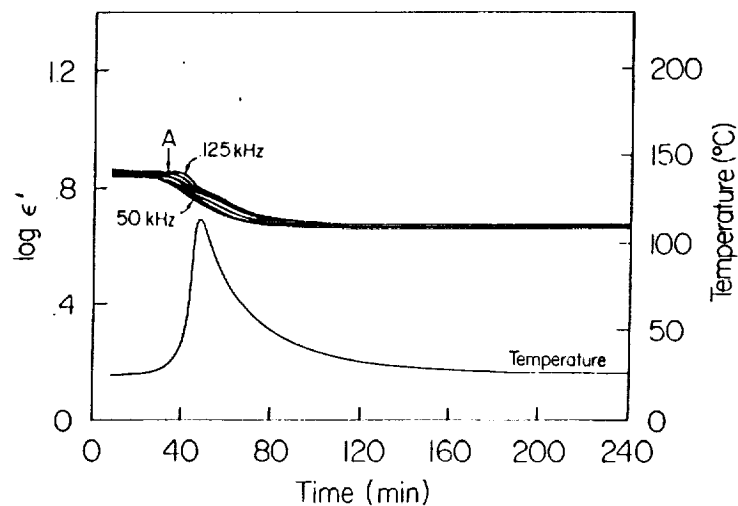

Fig. 5. Log ε' vs. time for a polyester resin crosslinking by a free radical mechanism. The point "A" denotes the onset of the polymerization process.
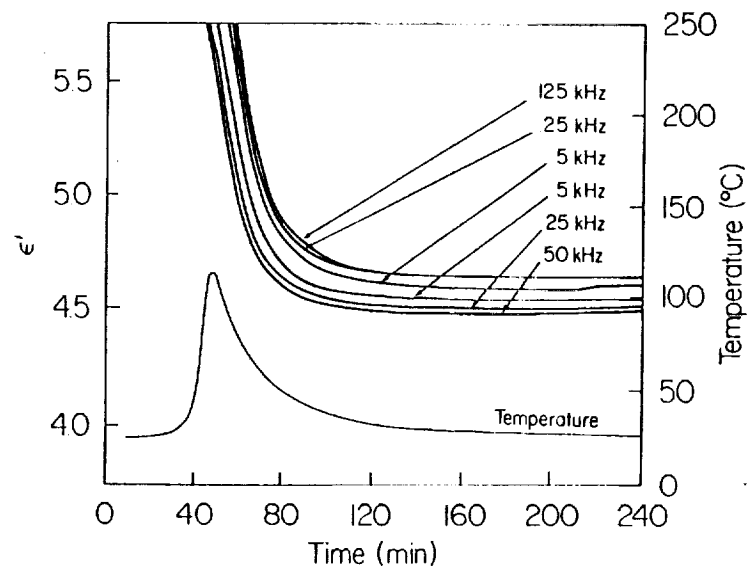
Fig. 6. An expansion of the curve in Fig. 5 showing the gradual drop to a steady value in ϵ' as the reaction terminates.
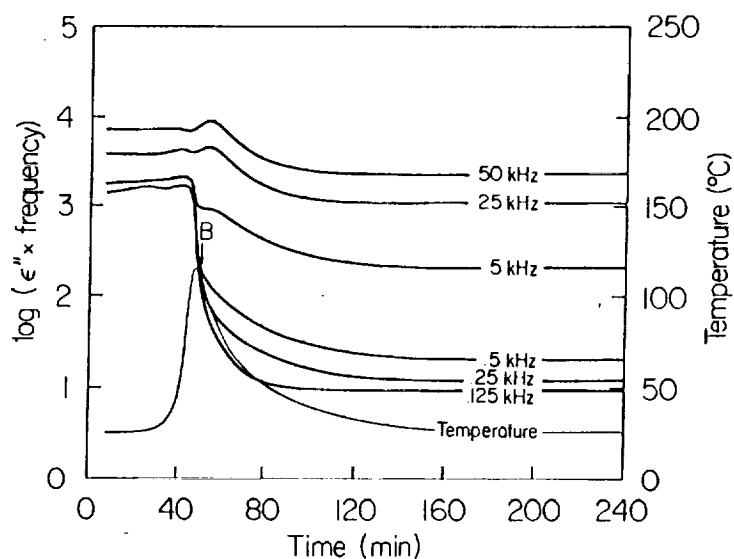

Fig. 7. Log ϵ'' x f vs. time for the reaction of Figures 5 and 6. At point "B" the low frequency curves diverge and ionic phenomena cease to be the major component in ϵ''.
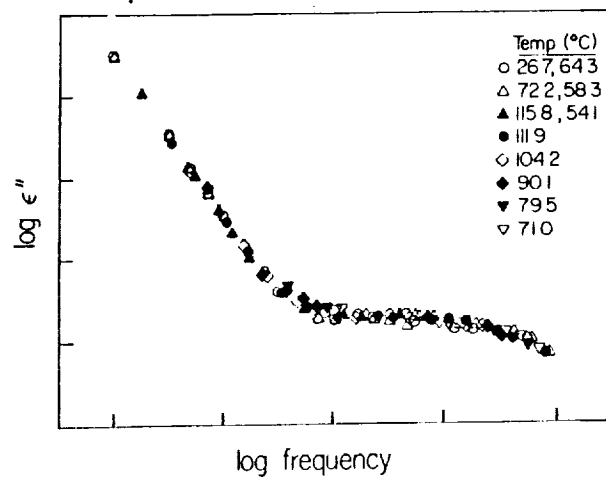

Fig. 8. A master curve for the polyester resin during cure.

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